

The Analysis of Trace Contaminants in High Purity Ethylene and Propylene Using GC/MS

Agilent Technologies/Wasson ECE Monomer Analyzer Application

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Abstract

A new product (Application 460B-00) from Agilent Technologies/Wasson-ECE uses a 5973N GC/MSD (gas chromatograph/mass selective detector) for the determination of trace levels of impurities that are moderate-to-low carbon-content such as oxygenates, mercaptans, sulfides, arsine, and phosphine in ethylene and propylene. This work describes the performance of Application 460B-00 with respect to linearity, repeatability, and limits of detection (for most compounds, low parts-per-billion). Compared to determinations with GC/FID (flame ionization detection) or GC/TCD

(thermal conductivity detection), the use of GC/MSD demonstrates comparable performance with respect to linearity and repeatability; for example, for mercaptans and sulfides (40–100 ppb) in the ethylene assay, correlation coefficients for calibration curves range from 0.992 to 1.000 and relative standard deviations range from 1.95% to 9.31% RSD. Compared to GC/FID for the range of contaminant analytes studied here, the sensitivity is increased 50-fold; compared to GC/TCD, the sensitivity is increased 5000-fold. While the sensitivity of MS detection is comparable to that of sulfur chemiluminescence detection for sulfur-containing compounds, MS has the same sensitivity for a broader range of compound types. Moreover, the use of MS detection provides specificity for positive identification of analytes. In Application 460B-00 the multipart assays are automated via "composite methods" [1]. The result is a tool that provides higher productivity and more key information about feedstock materials—both of which aid the polymer industry.

Introduction

For the polymer industry, the purity of ethylene and propylene monomer feedstocks is a high priority. Trace contaminants at the part-per-billion (ppb) concentration levels can affect yields dramatically by altering subsequent polymer properties and characteristics. Additionally, some trace impurities can irreversibly poison reactor catalysts. The competitive marketing strategies of monomer manufacturers include using new analytical technologies to guarantee lower and lower trace impurity levels.

Agilent Technologies/Wasson-ECE has focused on supplying integrated application products for the analysis of impurities in polymer feedstocks. One of the most recent products, Application 262-00, effectively combined the separate analyses for ethylene and propylene into a single analytical system [2].



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Application 262-00 employs a gas chromatograph (GC) with two separate flame ionization detectors (FIDs), two capillary columns, appropriate valving, and analytical methods to quantify very low levels of carbon monoxide and carbon dioxide by a methanizer FID and paraffins and olefins up to n-pentane by direct FID. Recently Agilent Technologies/ Wasson-ECE has expanded the capabilities of Application 262-00 by adding mass spectrometric (MS) detection in another product, Application 460B-00. This note describes applying GC/MS instrumentation and methods to analyze trace contaminants in polymer grade ethylene and propylene feedstocks.

Using GC/MS for Trace Contaminant Analyses

Mass Spectrometric Detection

Utilizing a mass spectrometer as the chromatographic detector provides significant benefits:

- Increased sensitivity
- Detection of analytes that do not produce a response with a FID
- Selectivity
- Positive identification through mass spectra

As the impact of trace levels of impurities becomes better understood, the need for increasing sensitivity in an analytical technique becomes more important. With flame ionization detection in Application 262-00, detection levels for carbon monoxide and carbon dioxide are on the order of 50 ppb while those for the paraffins and olefins up to n-pentane are about 1 ppm (parts-per-million).

MS detection is equivalently sensitive for these compounds. However, MS detection offers gains in sensitivity for those compounds with little or no FID response factors, for example, oxygenates, sulfur-containing compounds, and compounds with no carbon-hydrogen bonds (hydrogen sulfide, carbonyl sulfide, arsine, phosphine). Moreover, the selectivity afforded by MS detection is important because it provides confirmation that an analyte in question is indeed present by examining its mass spectrum (scan mode) or monitoring of multiple, specific ions (selected ion monitoring - SIM mode).

The GC/MS methods described here address a range of analytes beyond the scope of Application 262-00.

Gas Chromatographic Separation

Even with the inherent strengths of a mass spectrometer, some chromatography must still be employed. The detector's selectivity is not absolute, especially when simultaneously detecting components at vastly different concentrations (ppb versus bulk or percent levels). This means that the ppb contaminants must be reasonably separated from their ethylene or propylene matrix since coelution of a trace contaminant with the major matrix component yields a false positive with respect to the contaminant. Additionally, some of the analytes may interfere with each other by having the same molecular weight and/or fragment ions. Therefore, both chromatography and mass spectrometry are needed to provide identification.

For such a complex sample, no single gas chromatographic column provides adequate separation of the whole range of analytes and matrix components. Different selectivities of the capillary column stationary phases must be invoked to separate the various groups of very similar analytes. For this reason, Agilent Technologies/Wasson-ECE employs a multivalve, multicolumn approach to the chromatograph configuration.

Agilent Technologies/Wasson-ECE Application 460B-00

A new application product was developed to merge the advantages of MS detection with the necessary resolution afforded by appropriate chromatographic columns and automatic control of valved GC injections. The application includes multiple special inert capillary columns that do not irreversibly bind the analytes, addition of multiple valves, passivation of all components along the sample path (for example, valves, transfer lines), analytical methods for the GC/MS, and control software that coordinates the entire application.

In the multivalve, multicolumn approach, the sample (a gas or vaporized liquid) is purged through the injection valve. In this manner, the injection valve contains an aliquot of original sample, sized appropriately for the column to be used. The flexibility of programming both valve operation and chromatographic system pressures results in the sequential injection of the aliquot onto one of the multiple columns, the appropriate one being selected with a portion of the total analysis in mind. Each injection process defines a

method, resulting in a total of three sequential methods that comprise a full “composite method” to perform the selected assay. In executing a “composite method,” Agilent Technologies/Wasson-ECE's Composite Analysis Control Software (CACS) automatically sequences the sampling of the three separate aliquots of a feedstock sample, applying the appropriate GC/MS methods to each, and produces a combined, final report.

A Modular Approach to the Analysis of Trace Contaminants: Building on Application 460B-00

Application 460B-00 is a building block in a modular approach to providing the degree of automation appropriate to the users' needs. As described just above, Application 460B-00 is suitable for use in the laboratory where an analyst connects one pressurized sample container at a time to the system. However, a sampling system that automatically and sequentially samples pressurized sample containers is available from Agilent Technologies/Wasson-ECE; once the samples are installed, no user intervention is required.

Moreover, other products from Agilent Technologies/Wasson-ECE move Application 460B-00 from the laboratory to the process stream. In this configuration, there is a single sample source that is repetitively sampled. Since a “composite method” for Application 460B-00 takes about 1 hour per sample, knowledge of the bulk ethylene or propylene streams is available in a timely manner. This makes it possible to improve the quality of the product and reduce manufacturing costs associated with rework or waste disposal of large amounts of product that are out-of-specification due to contaminants in the bulk reactant.

Experimental

The instrumentation is outlined in Table 1. For the results presented here, an HP 5972 MSD was used. Table 2 outlines the impurities that were

characterized for the evaluation of Application 460B-00. Note that the ethylene and propylene analyses each require three separate GC/MS methods; these methods are not the same.

Table 1. The Instrumentation and Control Software for the Ethylene and Propylene Analyses in the Agilent Technologies/Wasson-ECE Product, Application 460B-00

Mass spectrometer	5973 MSD and later models
Gas chromatograph	6890 GC
GC Valve configuration	Provided by Agilent Technologies /Wasson-ECE. Sample loops of 100 µL and 500 µL
Columns	Provided by Agilent Technologies/Wasson-ECE: Wasson Part No. KZA and Wasson Part No. KZB
Software	<ul style="list-style-type: none"> • G1701 DA • Composite Analysis Control Software from Agilent Technologies/Wasson-ECE
GC/MSD Methods	Provided by Agilent Technologies/Wasson-ECE

Table 2. Analytes Used to Characterize the Performance of Agilent Technologies/Wasson-ECE Application 460B-00 for Impurities found in Ethylene

Component	Quant ion	Prepared analyte levels (ppb)
Methyl mercaptan	47	25, 35, 70, 115, 410
Ethyl mercaptan	62	15, 25, 55, 105, 315
Methyl-t-Butyl ether	73	10, 20, 38, 75, 223
Methanol	31	28, 55, 110, 205, 625
t-Butanol	59	12, 25, 45, 85, 265
Ethanol	31	18, 38, 75, 140, 433
isopropanol	45	15, 30, 78, 107, 335
sec-Butanol	45	15, 25, 45, 88, 270
1-Propanol	31	15, 30, 45, 110, 333
1-Butanol	56	12, 23, 58, 87, 270
Hydrogen sulfide	34	25, 100, 190, 575
Carbonyl sulfide*	60	15, 25, 75, 100, 310
Arsine	76	55, 115, 215, 440
Phosphine	34	50, 110, 205, 420

* For carbonyl sulfide in propylene, prepared analyte levels spanned 1–300 ppb

Standard mixtures of analytes in the bulk material were prepared by using permeation tubes from Agilent Technologies/Wasson-ECE; in this approach, concentration levels are determined by the flow rate of the bulk material. Mixtures of multiple trace analytes in the bulk material were prepared by plumbing multiple permeation tubes in series. The bulk ethylene was obtained from Alphagaz (“primary standard” grade). The analytes came from Chem Service.

Linearity for each analyte was determined in the usual manner (construction of calibration curves with the HP G1701 BA software) for the concentration levels noted in Table 2. For the repeatability studies, a single concentration level near the low end of the calibration range for each analyte was injected seven to eight times.

In general, detection limits (DLs) were determined in two ways. The first was to use the linearity and repeatability data to target the lowest concentrations at which the repeatability for five replicates would give 1% to 10% RSD (relative standard deviation). Samples at these concentrations were run in SIM mode (including automated peak detection and integration, and automated reporting) to provide actual minimum DLs.

The second was to run samples in SIM mode at concentrations estimated to yield responses having S/N (signal-to-noise) ratios of about 2.5. Integration was done manually, using the SIM mass chromatogram for each analyte.

Results

Figures 1 through 3 are examples taken from propylene and ethylene assays to show the type of output using the Agilent Technologies/Wasson-ECE product.

Tables 3 through 6 present the results of the experiments to characterize the performance of Application 460B-00 with respect to linearity, repeatability, and limits of detection (LOD).

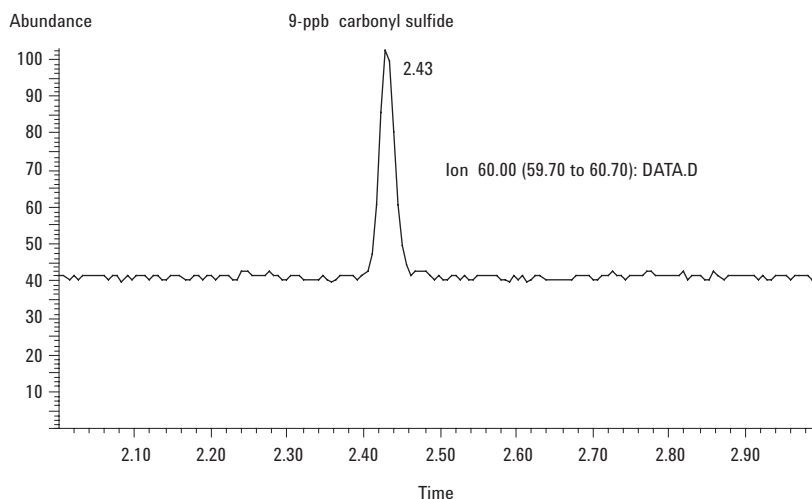


Figure 1. A section of chromatogram showing SIM detection for the determination of 9-ppb carbonyl sulfide in propylene at a customer's facility.

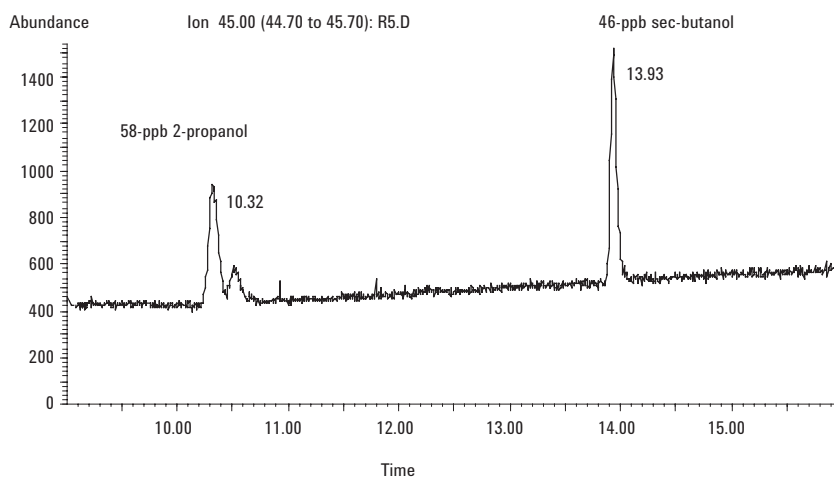


Figure 2. A section of chromatogram showing SIM detection for the determination of 58-ppb isopropanol and 46-ppb *sec*-Butanol in ethylene.

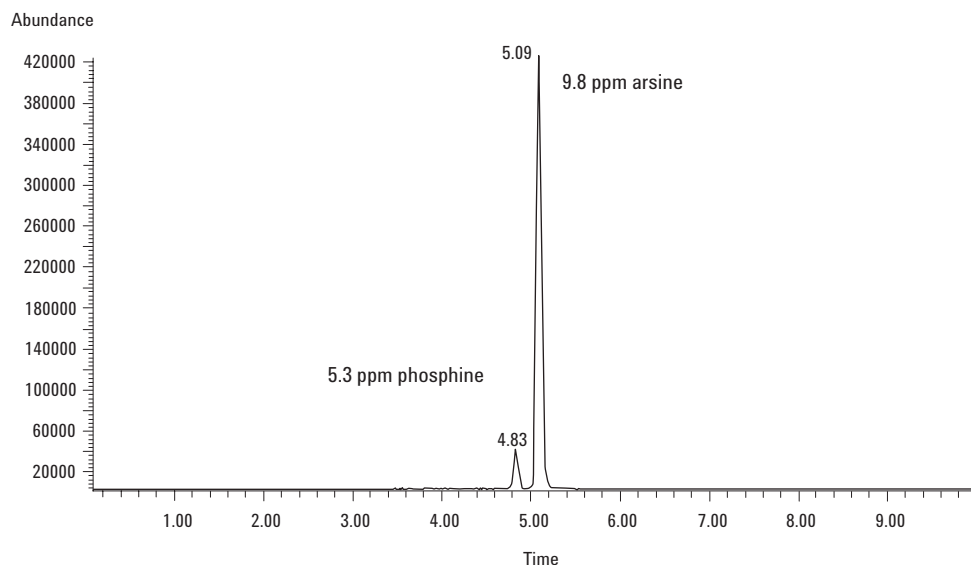


Figure 3. A section of chromatogram showing SIM detection for the determination of 240-ppb arsine in ethylene.

Table 3. Measures of Linearity for the Ethylene Impurity Analysis

	Concentration range	Number of calibration points	Correlation coefficient
Methyl mercaptan	25–410 ppb	5	0.999
Ethyl mercaptan	15–315 ppb	5	1.000
Methyl-t-Butyl-ether	10–223 ppb	5	1.000
Methanol	28–625 ppb	5	0.999
t-Butanol	12–265 ppb	5	1.000
Ethanol	18–433 ppb	5	0.999
isopropanol	15–335 ppb	5	1.000
sec-Butanol	15–270 ppb	5	1.000
1-Propanol	15–333 ppb	5	0.999
1-Butanol	12–270 ppb	5	0.998
Hydrogen sulfide	25–575 ppb	4	0.992
Carbonyl sulfide	15–310 ppb	5	1.000
Arsine	55–440 ppb	4	1.000
Phosphine	50–420 ppb	4	0.995

Table 4. Repeatability for Sulfur-Containing Compounds at ppb Concentrations Using the Agilent Technologies/Wasson-ECE Method for Determination of Ethylene Impurities

Sample number	Hydrogen sulfide	Carbonyl sulfide	Methyl mercaptan	Ethyl mercaptan
1	106.42	41.70	77.96	60.29
2	90.05	41.74	79.23	57.96
3	98.50	50.61	79.90	61.36
4	107.15	40.77	80.18	59.30
5	111.59	39.97	76.96	57.27
6	95.75	40.30	81.74	61.33
7	102.48	39.00	79.31	63.32
Average	101.71	42.01	79.33	60.12
Standard Deviation	7.44	3.91	1.55	2.11
% RSD	7.31	9.31	1.95	3.51

Table 5. Repeatability for Oxygenates at ppb Concentrations Using the Agilent Technologies/Wasson-ECE Method for Determination of Ethylene Impurities

Sample number	Methyl-t-Butyl ether	Methanol	t-Butanol	Isopropanol
1	48.25	160.91	54.62	73.03
2	46.33	141.46	51.91	65.61
3	48.58	79.02	49.19	61.98
4	48.38	122.15	48.99	62.01
5	44.91	98.72	51.29	70.76
6	46.52	126.15	53.50	67.15
7	48.92	127.03	54.32	66.80
8	45.35	127.09	52.54	64.90
Average	47.16	122.82	52.05	66.53
Standard Deviation	1.57	24.91	2.15	3.88
% RSD	3.33	20.29	4.12	5.83

Table 5 (continued). Repeatability for Oxygenates at ppb Concentrations Using the Agilent Technologies/Wasson-ECE Method for Determination of Ethylene Impurities

Sample number	Ethanol	sec-Butanol	1-Propanol	1-Butanol
1	86.10	52.38	63.47	58.22
2	81.44	54.94	67.02	60.33
3	82.82	53.65	62.64	59.24
4	75.90	52.05	67.34	54.88
5	95.45	51.00	68.12	59.47
6	80.51	54.19	66.98	59.89
7	85.32	54.20	65.37	58.13
8	84.86	53.50	71.87	55.85
Average	84.05	53.24	66.60	58.25
Standard Deviation	5.65	1.32	2.88	1.95
% RSD	6.73	2.47	4.32	3.35

Table 6. DLs for the Ethylene Impurity Analysis*

	Approach A** (ppb)	Approach B*** (ppb)
Methyl mercaptan	18	2
Ethyl mercaptan	14	3.5
Methyl-t-Butyl-ether	10	4
Methanol	28	20
t-Butanol	12	4
Ethanol	19	9
isopropanol	15	4
sec-Butanol	12	3
1-Propanol	15	4
1-Butanol	12	4
Hydrogen sulfide	26	10
Carbonyl sulfide	14 [†]	10
Arsine	10	7
Phosphine	50	30

* All values are in mole ppb or mole ppm.

** The lower DL was determined by the ability of the established integration parameters to detect the peak and integrate the peak properly.

*** Peak height at 2.5 times the noise. This peak will typically be integrated manually. This value was extrapolated from lowest concentration analyzed for each component.

† The DL for carbonyl sulfide in propylene using Approach A was found to be 5 ppb.

Summary

The performance of Agilent Technologies/Wasson-ECE's Application 460B-00 was evaluated for linearity, repeatability, and LOD for trace contaminants in ethylene. The results show that impurities in ethylene can be precisely determined to the low ppb levels for compounds that are not amenable to either trace analysis by GC/FID (where the typical LOD for the cited compounds range from 50 ppb for carbon dioxide and carbon monoxide to ppm for paraffins and olefins) or by GC/TCD (where the sensitivity is 5000-fold lower).

Application 460B-00 can also be used to determine trace contaminants in propylene as demonstrated by the carbonyl sulfide in propylene results (Figure 1). Additionally, it should be applicable to other analytes that were not studied in this work: acetone, 4-methylcyclohexene, 4-ethyl-cyclohexane, and aromatics.

By having "composite methods" that automatically perform the appropriate sequences of sampling plus methods, manual intervention is minimized for each sample. In the laboratory, the operator needs only to install each pressurized sample source from one sample to another and start the composite method. A greater degree of automation with less intervention per sample is possible by adding an automatic sampler product.

The analysis times for the "composite method" are wellmatched to the needs of polymer manufacturers for feedstock assays. For example, the full composite

method for the ethylene assay takes about 1 hour. Typically in an off-line analysis approach, manufacturing facilities obtain samples of the feedstock and submit them to the laboratory for analysis. The 1-hour analysis time is a fairly small part of the total turn-around-time (several hours) to get analytical information back to the production line.

By moving the Application 460B-00 online using other products from Agilent Technologies/Wasson-ECE, the polymer manufacturer could analyze feedstock materials about once per hour to maintain maximum productivity and quality while minimizing loss of product and/or rework.

The Agilent Technologies/Wasson-ECE product, Application 460B-00, provides reliable results in a timely manner for bulk ethylene and propylene feedstock fluids with a minimum of manual intervention for the determination of impurities that have minimal carbon content and/or are highly oxygenated.

References

1. 460B-00
2. 262-00

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